Center For Nanoscale Materials - Proposal #xxxxx

Proposal Title: Surface lattice plasmon interaction with excitons in gain medium

Principal Investigator/Spokesperson

Badge No.	Title	First Name	Last Name	Affiliation	Phone	Email	First Time User
81398	Prof.	x	x	x University	x	x	N

Collaborators

Badge No.	Title	First Name	Last Name	Affiliation	Phone	Email	Coming to CNM?	First Time User
x	Mr.	x	x	x University - Ph.D. Student	x	x		
x	Ms.	x	x	x University - Ph.D. Student	x	x		N

General information

Contact Name: Richard Schaller

Selected Theme(s): Nanophotonics
Field(s) of Research: Materials sciences (Including condensed matter physics & materials chemistry), Optics
Funding Source(s): NSF
How many visits are needed to complete the experiment? 12.0
How many days per visit? 1.0
Timeframe for entire project in months? 12.0
Are you collaborating with CNM personnel in performing this work or experiment? No
Do you plan to perform this work or experiment with assistance from CNM personnel? Yes
If this is a proprietary proposal, is it acceptable to disclose scientific content of this proposal to CNM personnel prior to experimenta Yes
Have you contacted CNM scientific staff to discuss the feasibility of your proposal? Yes
Will the data collected be considered proprietary? No
How did you first hear about the applicability of CNM to your research?
A colleague, supervisor or advisor not affiliated with the CNM

Abstract

Plasmons are collective oscillations of electrons in the conduction band of metallic nanostructures at optical frequencies. The field of nanoplasmonics has led to a number of applications, including enhancement of photovoltaic devices, ultrasensitive bio-detection, and surface enhanced raman spectroscopy. To further advance the application of plasmonics for nanoscale light sources, we are interested in the interaction between plasmonic structures and gain materials. The specific type of plasmonic structures under examination exhibits surface lattice plasmons, wherein light is trapped in the plane of nanostructures, and the electric dipoles of individual nanoparticles oscillate in phase.[1] According to Fermi's golden rule, plasmonic structures will modify the optical local density of states, enhancing the spontaneous emission rate of emitters by the Purcell factor.[2] Furthermore, surface lattice plasmon modes suppress radiative loss in the metallic structures by canceling out scattering linewidth of individual particles. With these two features, gain media such as quantum dots (QDs) can be efficiently pumped and will exhibit enhanced fluorescence, amplified spontaneous emission and even lasing action.

This ability of surface lattice plasmon modes to enhance the fluorescence of nearby emitters, could also support a major breakthrough for carbon nanotubes (CNTs) as gain media. CNTs have been widely studied for their structural and electronic

properties, but they also display potentially useful optical properties that have yet to be developed. Certain species of CNTs act as near-IR emitters of low efficiency. Studying exciton-plasmon interactions in CNTs coupled to plasmonic arrays may allow for enhanced CNT emission leading to new applications for CNTs as a gain medium.

Description of Research

1. Describe the scientific or technical purpose and the importance of the proposed research.

Scientifically, we are interested in how energy transfers from gain media to the nanoplasmonic structures and how gain media use the properties of surface lattice plasmon modes as an energy output channel. Compared to surface plasmon polaritons in continuous metallic films and localized surface plasmons in individual nanoparticles, surface lattice plasmon modes of nanoparticle arrays can not only highly concentrate light on subwavelength scale, but also confine light in the plane of the substrate and suppress the dissipative losses of the system. Thus, nonlinear effects such as amplified spontaneous emission and coherent lasing action will be achievable with a surface lattice plasmon mode that provides stable optical feedback. This interaction between nanoparticle arrays and quantum emitters will increase the decay rate of excitons and the emission will follow the surface lattice plasmon mode dispersion. This research will provide us with insight regarding energy dynamics of plasmon-exciton systems in the strong coupling regime. We are interested in both quantum dots (QDs) and carbon nanotubes (CNTs) as gain media.

QDs have high photostability and well-controlled absorption and emission bands due to their spatial confinement, so they have been widely used in biomedical imaging[3], LEDs[4], and photovoltaics[5]. Compared to organic laser dye, QDs have a higher quantum yield and photobleaching resistance under high external pumping, which makes them ideal gain media for plasmonic lasing applications. Previous studies demonstrated large enhancement of fluorescence efficiency[6] or increase of decay rate of spontaneous emission[7] when coupled to plasmonic structures. However, lasing action is hard to observe within QD-plasmonic structures because efficient optical feedback and decreases in losses are essential to using QDs as gain medium in nanolasers. A surface lattice plasmon mode that supports ultrafast dynamics and high mode quality and suppresses losses enables us to explore the strong coupling between QDs and plasmonic structures. Notably, the excitons in QDs are delocalized Wannier excitons, whose interaction with plasmons in the strong coupling regime has not been fully studied.

CNTs have many properties of an ideal gain material: they are robust against photo-bleaching, display an assortment of emission frequencies based on chirality, and support scalable processing methods.[8,9,10,11] However, low photoluminescence efficiency (<0.1%) has largely prevented the application of CNTs as emitters in photonic devices such as lasers and LEDs.[12,13] In comparison, many laser dyes used as gain media in conventional laser systems possess quantum efficiencies well over 50%, thus CNTs emission requires several-fold enhancement before becoming a viable gain medium candidate. One potential solution is to couple the emission of CNTs to the surface lattice plasmon mode of gold nanoparticle arrays. The plasmonic nanoparticle arrays would provide a high optical local density of states for enhancing CNT emission, and such plasmon-exciton system involving CNTs have not been well studied.

2. Describe and justify the relevance of the proposed research to nanoscience/nanotechnology.

We use scalable nanofabrication techniques for creating plasmonic particle arrays over large areas (>1 cm^2) exhibiting extraordinary optical responses. This expertise allows us to conduct research on the fundamental science of plasmonic systems, whose scalability make them practical for nanoscale device applications such as lasers and LEDs. QDs are materials with nanoscale spatial confinement, whose absorption and emission properties can be controlled by their growing process. This flexibility has led to studies about their applications such as fluorescence tagging in biomedical system[3], LEDs[4], and photovoltaics[5]. Specifically, plamonic lasers based on quantum-confined semiconductor material have been studied. However, they usually use metallic films as their plasmonic structure. To decrease the losses in their systems, they applied a low temperature environment[14] or an internal reflection optical design[15]. Surface lattice plasmon modes in the metallic nanoparticle arrays have high optical mode quality by suppressing the loss which allows us to operate at room temperature and use simple structure designed for targeted working wavelength. The coupling of delocalized excitons in QDs with surface lattice plasmons is not well understood; so for future applications, it is important to study the fundamental energy dynamics of this hybrid system. Likewise, CNTs have been well studied in some respects, but their fluorescent properties still possess significant unlocked potential that is likely accessible when coupled to plasmonic structures.

3. Provide a justification for requesting CNM resources and the particular capabilities chosen, especially if you have similar instruments in your institution.

To study the energy transfer from gain media into plasmonic structures, it is critical to measure the decay rate of gain media using transient absorption setups, which is not feasible with our own instrumentation.

To efficiently pump our gain media, we need tunable femtosecond light sources around 500 nm for CdSe/CdS QDs, 900 nm for PbS QDs and around 570 nm and 990 nm for CNTs.[8] However, the only laser source we have in our lab is an 800 nm pulsed laser source.

Moreover, the emission detection is out of the range of our spectrometers as PbS quantum dots and CNTs show emission beyond 1000 nm.[8] In order to measure these signals, we need a near-IR device.

The TCSPC setup at the CNM has a tunable light source ranging from 390 nm to 1000 nm which will meet our exciton wavelength requirement of gain medium. Furthermore, the CNM is equipped for detecting near-IR emission.

4. Describe your samples and procedures, and explain the basis for the time request(s).

A typical sample of our surface lattice plasmon system is Au or Ag nanoparticles in a square array on top of a glass substrate, with Cr or Ti used as an adhesion layer. For QDs, we will spincast photoresist onto it and create a microchannel. QDs samples are dissolved in organic solvent and sealed into the microchannels. In the case of CNTs, gelatin is used as a dispersion medium, and this solution is then formed into a thin film coating the Au nanoparticle arrays using the doctor blade method. Sample preparation in our lab will take one week.

Then, we will use TCSPC microscopy to pump the system at its best absorption wavelength, and detect the emission signal. Usually, QD systems need excitation at 500 nm to 600 nm and 850 to 900 nm ranges, whereas CNTs require excitation at 570 nm and 990 nm.[8]

Transient absorption will be applied to measure decay rate of the gain medium with and without the plasmonic nanostructures.

Ideally, we need one visit to characterize each system. For each visit, we need two days on TA and TCSPC setups, respectively. However, owing to the imperfection caused by nanofabrication and possible damages to the samples under laser exposure, we may need to remake new samples for these measurements. Also, we would like to try different types of QDs and CNTs samples using different CNT chiralities or dispersion media other than gelatin.

In total, we plan to make 12 visits and the entire proposed project will span over 12 months.

5. Describe all of the participants' previous experience relevant to the proposed research AND any preliminary research results obtained.

All participants in this proposal have ample experience with nanofabrication methods for producing plasmonic nanoparticle arrays studied in the proposed research projects. The scalable fabrication techniques involve phase-shifting photolithography, SANE/inSANE embossing, etching, e-beam deposition, and PEEL[16]. We have characterized the linear optical properties of our fabricated metal arrays using a homemade rotational stage to identify the quality and dispersion properties of the surface lattice plasmon mode, and UV-Vis measurements to confirm spectral overlap of the surface lattice mode with the emission of various gain media. The prototype system that has been studied in our group is dye molecules within a plasmonic structure.[17] The participants have hands-on femtosecond pulse laser experience for pumping and measuring emission from this active plasmon system. The absorption and emission spectra of CNTs have been measured using the Horiba Jobin-Yvon Nanolog Spectrofluorimeter at the CNM as part of Proposal No. This instrumentation allowed for the production of preliminary photoluminescence maps for solutions containing several chiralities of CNTs.

6. Describe briefly the outcome of prior allocated proposals to the CNM that are not included above. This is mandatory if this proposal is a continuation of a previous CNM proposal. Include:

- **a. The previous proposal number(s).**
- **b. Restate the purpose.**
- **c. Briefly summarize the results and the role that CNM played.**
- **d. Provide a list of your publications and presentations that contain data obtained from using the CNM.**

As part of CNM Proposal No. xxxxx, our group examined plasmon-exciton energy transfer in systems of plasmonic nanoparticles coupled to fluorescent dyes. Transient absorption measurements carried out at the CNM demonstrated enhanced decay rates of excited near-IR dyes due to strong coupling with the plasmonic gap mode of gold bowtie dimers [I could not get any significant result using the CNM equipment due to the huge gain medium slab we use.

The resulting publication is currently under preparation. Also, the transient absorption measurements on decay rate of nanoparticles with various shapes revealed the origin of saturated absorption behavior for nanoparticles under high pump power, and this publication is currently under preparation by PhD candidate x.

We also have an ongoing nanofabrication proposal (No. xxxxx) at the CNM as a complement to the new active plasmonics proposal we are now submitting....

7. References, including relevant publications (Max 2000 characters)

[1] S.Zou and George C. Schatz, Journal of Chemical Physics 121, 12606 (2004).
[2] E. M. Purcell, H. C. Torrey, and R. V. Pound, Physics Review 69, 37 (1946).

[3] X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu,S. S. Gambhir and S. Weiss, Science 307, 5709,538 (2005).
[4] J.S. Steckel, S. Coe-Sullivan, V. Bulovi and M.G. Bawendi, Advanced Materials 15, 21, 1862 (2003).
[5] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina and E. H. Sargent, Nature Materials 4, 138 (2005).
[6] J. Song, T. Atay, S. Shi, H. Urabe and A. V. Nurmikko, Nano Letters 5, 8, 1557 (2005).
[7] O. L. Muskens, V. Giannini, J. A. Sánchez-Gil and J. Gómez Rivas, Nano Letters, 7, 9, 2871 (2007).
[8] S. Ghosh, S. M. Bachilo, R. A. Simonette, K. M. Beckingham, and R. B. Weisman, Science 330, 1656 (2010).

Please see attachment for remaining references.

Capabilities and Usage

Nanophotonics

- Transient absorption spectroscopy
  - Days Per Visit:
  - Total Visits: 5
  - Total number of days of use: 5
  - Near-IR probe
  - Visible probe
- Time-resolved emission spectroscopy
  - Total number of days of use: 5
  - TCSPC Microscopy
    - Number of times of use:
    - Total Hours Of Usage:
  - Near-IR TCSPC
  - Time-correlated single photon counting (TCSPC) spectroscopy
- Visible and near-IR microscopy
  - Total number of days of use: 2
  - NEAR-IR detection
  - Visible detection
  - Laser illumination
  - Lamp illumination

Safety

Will the proposed activity involve the use of carcinogens, mutagens, or reproductive hazards at the Argonne facility?
No

Will the proposed activity involve the use of biohazards at the Argonne facility?
No

Will the proposed activity involve the use of human tissue/materials/cells at the Argonne facility?
No

Will the proposed activity require the transport of USDOT Select Etiological Agents to the Argonne facility?
No

Will the proposed activity involve the use, characterization, or other handling of radioactive materials at the Argonne facility?
No

Will the proposed activity require the use of user-supplied equipment at the Argonne facility?

No

Will the proposed activity involve significant hazards (at the Argonne facility) that are not identified above?

No

Attachments

CNM_SurfaceLatticePlasmon_references.pdf

References

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